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THE CRYSTAL STRUCTURE OF ZINC 8-HYDROXYQUINOLINATE DIHYDRATE

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SUMMARY

The crystal structure of zinc 8-hydroxyquinolinate dihydrate, $Zn(C_9H_6OH)_2 \cdot 2H_2O$ has been determined by single crystal methods. The unit cell is monoclinic with

$a = 11.28A^\circ$ $b = 5.42A^\circ$ $c = 13.16A^\circ$ $\beta = 106^\circ 18'$

The space group is $P_{2_1/a} - C^5_{2h}$ and there are two molecules per unit cell.

Atomic positions were determined by Fourier projections and were refined by a three-dimensional Fourier electron-density synthesis and by the method of least squares. Structure factors were obtained from visually estimated intensities on Weissenberg photographs taken with Cu Kα radiation.

The molecule, with the exception of the water molecules, is essentially planar. Including the water molecules, there is a sort of distorted octahedral arrangement of bonds around the central zinc ion. The Zn-O and Zn-N bond lengths are 2.05A° and 2.06A°, respectively, while the Zn-OH_2 bond length is 2.27A°.

INTRODUCTION

This report is the second in a series from these Laboratories dealing with the crystal structure of organic reagents of analytical importance and the complexes they form with metallic ions. The first report (Merritt and Lanterman, 1952) concerned the structure of dimethylglyoxime. Unlike dimethylglyoxime which is quite selective in its action, 8-hydroxyquinoline reacts with a large number of different ions.

Experimental Technique, Unit Cell and Space Group

Single crystals of zinc 8-hydroxyquinolinate dihydrate are quite difficult to prepare. The zinc salt is precipitated from an acetic acid solution by addition of a slight excess of a 5% solution of 8-hydroxyquinoline in 12% acetic acid and subsequent neutralization with dilute ammonium hydroxide. The precipitate consists of very small crystals which give a powder pattern identical with that of powdered single dihydrate crystals. This finely crystalline precipitate is washed thoroughly with hot water to remove any excess 8-hydroxyquinoline and then

is dissolved in pyridine. Water is added to the pyridine solution, kept at about 80°C until a precipitate begins to form. The precipitate is redissolved by adding a little pyridine and the whole solution is cooled slowly, in an oven, to room temperature. Cooling over a period of two or three days yields crystals of usable size, however, most crystals are lamellar twins, twinning plane (001). Only rarely does one find a good single crystal. The crystals are pale yellow and translucent. The refractive indices were determined by the usual immersion methods to be

$$a = 1.650 \pm 0.002 \qquad \beta = 1.78 \pm 0.02 \qquad \gamma = >1.82$$

Sign of refraction = -

So few well-formed single crystals were available that the orientation of the indicatrix was not thoroughly established; however, $b = \gamma$

The unit cell dimensions were obtained from oscillation photographs and from Weissenberg photographs employing the method of ω separations (Buerger 1942). The results are

$$a = 11.28A^\circ \qquad b = 5.42A^\circ \qquad c = 13.16A^\circ \qquad \beta = 106^\circ 18'$$

The density by the flotation method is 1.682 g./cm.$^{-3}$ which gives 1.98, i.e., 2 molecules per unit cell. By an unusual coincidence in this crystal, pointed out by Hughes (1950), there exists a good check on the consistency of the values of a, c and β. On Weissenberg photographs of twinned crystals rotated about the [010] axis, every third layer where h = 0, 6 or 12 consists of single spots whereas otherwise the spots are doublets. Only when all of the spots begin to be resolved into $K\alpha_1$ and $K\alpha_2$ doublets are these spots on every third layer resolved into three or four spots. This indicates that the reciprocal lattice moves $2\sigma^*$ in going $6a^*$ so that using the values of a and c found previously:

$$\cos\beta = \frac{c}{3a} = \frac{8}{3c} \qquad (1)$$

$$\text{and } \beta = 106^\circ 36' \qquad (2)$$

This value of β checks well with that found above.

Complete sets of equi-inclination Weissenberg photographs about the [100] and [010] axis were taken for intensity estimation. The crystals used were roughly 1 mm. long by 0.2 mm. in diameter. No corrections for absorption were made. Copper Ka radiation filtered through nickel was employed and relative intensities were estimated visually by comparison with a standard intensity strip prepared by making a series of timed exposures of the (202) reflection. The multiple film technique of Robertson (1943) was employed using four sheets of Eastman No-Screen X-ray film and a factor of 3.7 for the decrease in intensity on passage of the beam through one layer of film. The usual corrections for the Lorentz and polarization factors, the oblique penetration of the film by the X-rays for non-equatorial layer photographs, and the relative time factor of Cox and Shaw (1930) were applied. The zero layer Weissenberg film about [100] was taken as the standard film and by cross calibration all intensities were reduced to this common level. Relative $|F_o|$ values were calculated.

Systematic absences were noted for h0l when h is odd

0k0 when k is odd

h00 when h is odd

with the single exception that an extremely weak reflection was observed at the

place where (010) should occur. If this is a true reflection then the space group could be $P_{2_1/a}$ or P/c. The external morphology of the crystal shows a two-fold axis of symmetry which would fix the space group as $P_{2_1/a}$. However, it is impossible to pack the required two molecules satisfactorily in the unit cell in this space group with the short b axis existing in this crystal. Therefore it appears certain that the correct space group is $P_{2_1/c} - C^5_{2h}$ and that the very weak (010) reflection is most probably due to an internal reflection or perhaps to some slight disorder in the [010] direction.

Determination of Atomic Positions

A Patterson projection, Figure 1, upon (010) is sufficiently well resolved to yield a trial structure. Contour lines in Figure 1 are drawn at arbitrary levels of 100, the zero contour being dotted. Crosses represent the ultimate positions of projected vectors between the zinc atom and the other atoms of the same molecule.

Structure factors, F_{h0l}, were calculated for this trial structure. Atomic scattering factors were taken from the Internationale Tabellen with corrections applied to those for zinc due to dispersion of the K electrons (James 1950). Since the zinc atom contributes to all of the 182 terms of this zone, nearly all signs are positive. Actually the signs of 154 terms appeared to be definitely fixed so that they could be included in the first Fourier projection. Three Fourier projections served to refine the x and z parameters. Only a very few of the weaker terms changed sign in the process of refinement. The third Fourier projection on (010) is shown in Figure 2. Contours are drawn at intervals of 1e $A^{\circ -2}$ except near the origin where the contour interval is $5 A^{\circ -2}$. The one electron contour is dotted and the crosses show the final positions of the projected atomic centers after the structure determination was completed. For comparison purposes the final structure is shown as if projected on (010) in Figure 3.

After each projection a temperature and scale factor was determined by the method of least-squares using the following equation to represent the relationship between Fo and Fc.

$$k|Fo| = |Fo| \exp - B\left(\frac{\sin\theta}{\lambda}\right)^2 \qquad (3)$$

The value of $R = \sum |Fo - Fc| \div \sum |Fo|$ decreased from 0.81 to 0.18 and 0.164 during the process of these refinements. Centers of peaks were determined by the method of Carpenter and Donohue (1950). After the x and z parameters were established by the projection on (010) an estimate of the tilt of the molecule was made by measuring the bond lengths in the benzene and pyridine rings, in projection, and comparing these lengths with the expected values. It was estimated that the molecule was tilted about 49° around an axis nearly perpendicular to [100] and lying in the (010) plane. From this information the y parameters were estimated and the structure factors for all reflections were calculated. By trial and error it was discovered that better agreement between $|Fo|$ and $|Fc|$ could be obtained if the angle of tilt were increased to 50°. At this point it was decided to carry out the refinement with a three-dimensional Fourier synthesis, since ordinary projections along [100] or [001] would not show many resolved atoms.

Slight corrections were obtained from the three-dimensional density function. It appears that the molecule is tilted about 50.5° around an axis inclined 94° to [100] and also which makes a slight angle of 3 3/4° with the (010) plane.

A least-squares refinement of the parameters according to the method of Hughes (1941) completed the structure determination. All of the 1636 reflections within the region investigated were included in this treatment. Only the diagonal terms were calculated and used in solving the normal equations. The final corrections from the least-squares method averaged 0.025A° per parameter with a

maximum of 0.10Å° in the z parameter of the C_1 atom. Final parameters for the atoms are given in Table I. The final values of $|F_o|$ and F_c are given in Table II. The final value of B, the exponent in the temperature factor expression, was 2.23×10^{-16} cm^2.

There are 213 unobserved reflections. If those for which F_c is below the minimum observable value for the region of the film in which the reflection should occur are not counted but those for which F_c would indicate the reflection should have been observed are taken at the minimum observable value of F_o, then R turns out to be 0.226. If these 213 reflections are left out altogether R would be 0.219.

The calculations of the Fourier density functions, structure factors and least-squares refinement were carried out with the aid of I.B.M. machines (Donohue and Schomaker, 1949; Shaffer, Schomaker and Pauling, 1946).

TABLE I

Atomic Parameters of Zinc 8-hydroxyquinolinate Dihydrate

Atom	Fraction of Cell Edge		
	x	y	z
C_1	0.158	0.286	0.194
C_2	0.204	0.326	0.303
C_3	0.167	0.175	0.372
C_4	0.037	0.832	0.396
C_5	0.951	0.646	0.350
C_6	0.909	0.623	0.244
C_7	0.952	0.770	0.178
C_8	0.041	0.958	0.225
C_9	0.082	0.978	0.336
O_1	0.912	0.762	0.076
O_2	0.156	0.734	0.008
N_1	0.079	0.104	0.156
Zn	0.000	0.000	0.000

Discussion of Structure

The dimensions of a single asymmetric unit are presented in Figure 3 and Table III. Because of the presence of a heavy atom in the structure the positions of the lighter atoms cannot be fixed as accurately as desired. It seems probable that errors in bond distances between light atoms may be as high as 0.06 to 0.08A° judging by the bond lengths in the benzene and pyridine ring and little weight should be placed on the irregularities in the bond lengths in these rings. The lengths of the bonds around the zinc atom, which are the most interesting in this crystal, are undoubtably more precise due to the exact knowledge of the position of the zinc ion and should not be in error by more than about 0.03 to 0.04A°.

It would appear that the major distortions in bond angles which results from formation of the five-membered ring are in the angles around the zinc ion and around the nitrogen atom. The Zn - N - C_8 angle has been decreased significantly from the expected angle of 120°.

The arrangement around the zinc atom is that of a distorted octahedron. This is shown schematically in Figure 4. The bond angle of 79.8° between the oxygen, zinc and nitrogen atoms of the main part of the molecule probably represents a sort of compromise due to the rigid structure of the organic chelating molecule and the inability to approach closer to the zinc atom without causing too short bonds and too great a negative charge upon the zinc atom. A somewhat similar distorted octahedral arrangement is found in nickel glycine dihydrate (Stosick, 1945). If the ligands were free to move as necessary then a more regular octahedral structure would be expected such as was observed by Tang and Sturdivant (1952) in manganese chloride dihydrate-hexamethylene diamine complex.

The zinc atom has a closed third electron shell and therefore the bonding of the six groups must be through use of the 4s, $4p^3$ and $4d^2$ orbits. This would be similar to the case of the above mentioned manganese complex where magnetic susceptibility measurements have shown five unpaired electrons. There is undoubtably considerable ionic character in these bonds.

From the normal covalent radii ascribed to oxygen (0.66A°) and to nitrogen (0.70A°) and the Zn-O_2 and Zn-N bond distances in this crystal, it appears that the octahedral covalent radius of the zinc atom is about 1.38A°. Pauling (1945) lists 1.31A° as the tetrahedral covalent radius of zinc. The increase of about 0.07A° seems reasonable if the unstable 4d orbitals are involved at all.

The water molecules are much less firmly attached to the zinc atom than is the organic molecule as shown by the greater Zn-O_2 distance and confirmed by the fact that the compound loses these water molecules on drying above 135°C. The anhydrous complex is undoubtably tetrahedral since Liu and Bailar (1951) have been able to resolve the anhydrous zinc complex of 8-hydroxyquinoline-5-sulfonic acid into optically active isomers. Lundy (1948) has shown that the copper 8-hydroxyquinolinate complex exists in two forms, an anhydrous form with space group $P_{2_1/a}$ and four atoms per unit cell and a dihydrate isomorphous with the zinc complex. According to this observation, there is no reason why the anhydrous form, at least of the copper complex, should not be tetrahedral. It is interesting to note that the resolved compounds of Liu and Bailar are easily racemized on standing in water which might indicate that they pick up two water molecules and revert to the structure shown in this report.

The molecules in zinc 8-hydroxyquinolinate dihydrate show no unusually close approaches. The smallest intermolecular distance is 3.45A° between adjacent water molecules. The closest approach of carbon atoms is 3.47A°. These distances

eliminate the possibility of hydrogen bonding and indicate that molecular binding in the crystal is mainly through van der Waals forces.

The hydrogen atoms, which altogether contribute 8% of the scattering matter of the unit cell, were neglected entirely in this determination. Inclusion of the hydrogens would probably improve slightly the agreement between observed and calculated structure factors. It is also probable that an anisotropic temperature factor would materially improve the agreement. A root-mean-square displacement of the atoms of 0.17A° is indicated from the value of B in the temperature factor expression.

The atoms of the 8-hydroxyquinoline molecules and the zinc atom all lie in a plane within the limits of experimental error except perhaps for the oxygen atom, O_1, which seems to be about 0.10A° below the least-squares-best plane. If the five-membered ring alone is considered, none of the atoms in this ring are more than 0.05A° from a plane. The equation of the least-squares-best plane for the whole assymetric unit in terms of the unit cell vectors is

$$a - 0.3994b - 0.2554c = 0 \qquad (4)$$

The average deviation of atoms from this plane is 0.03A° and the maximum deviation is 0.10A° for the oxygen atom O_1.

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TABLE III

Interatomic Distances and Angles in

Zinc 8-Hydroxyquinolinate Dihydrate Crystal

Bond	Distance	Bonds	Angle
$Zn-O_1$	2.05A°	O_1-Zn-N	79.8°
$Zn-N$	2.06	O_1-Zn-O_2	94.6
$Zn-O_2$	2.27	$N-Zn-O_2$	92.7
$N-C_1$	1.33	$Zn-N-C_8$	111.8
C_1-C_2	1.38	$N-C_8-C_7$	116.1
C_2-C_3	1.40	$C_8-C_7-O_1$	117.4
C_3-C_9	1.42	C_7-O_1-Zn	114.3
C_8-C_9	1.40	$N-C_1-C_2$	120.9
C_8-N	1.37	$C_1-C_2-C_3$	119.9
C_4-C_9	1.32	$C_2-C_3-C_9$	121.1
C_4-C_5	1.41	$C_3-C_9-C_8$	113.5
C_5-C_6	1.34	C_9-C_8-N	125.1
C_6-C_7	1.37	C_8-N-C_1	119.0
C_7-C_8	1.44	$C_7-C_8-C_9$	118.8
C_7-O_1	1.29	$C_8-C_9-C_4$	121.0
		$C_9-C_4-C_5$	120.1
		$C_4-C_5-C_6$	120.6
		$C_5-C_6-C_7$	121.6
		$C_6-C_7-C_8$	117.8
		$C_6-C_7-O_1$	124.4
		$Zn-N-C_1$	128.9
		$C_3-C_9-C_4$	125.6

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TABLE II

Observed and Calculated Structure Factors

The reflections in the following table are listed in groups with h and k constant in each group. The first column gives the l index, the second gives the calculated structure factor, and the third gives the observed structure factor. All values of structure factors have been multiplied by ten to eliminate decimals.

001

l	Fc	Fo
2	-36	57
3	800	920
4	273	336
5	767	1005
6	589	708
7	146	129
8	279	340
9	236	320
10	235	315
11	271	326
12	299	375
13	274	361
14	150	173
15	108	133
16	103	94

011

l	Fc	Fo
1	150	112
2	95	84
3	264	241
4	153	127
5	230	258
6	168	170
7	-124	112
8	-121	60
9	-11	<21
10	-21	53
11	-154	126
12	-18	23
13	120	80
14	-31	30
15	24	25
16	2.0	< 8

021

l	Fc	Fo
0	-204	189
1	39	51
2	100	46
3	209	227
4	318	336
5	132	127
6	216	221
7	218	219
8	268	267
9	315	345
10	-22	73
11	-58	28
12	100	136
13	61	97
14	77	115
15	49	71

031

l	Fc	Fo
1	24	17
2	-264	232
3	-249	230
4	-34	60
5	49	53
6	71	50
7	-72	80
8	-133	129
9	61	50
10	135	129
11	62	71
12	21	23
13	-25	19
14	-45	26

041

l	Fc	Fo
0	319	327
1	424	409
2	337	312
3	227	244
4	288	246
5	224	223
6	225	361
7	104	62
8	25	46
9	197	216
10	228	416
11	176	373
12	138	315
13	72	85

051

l	Fc	Fo
1	80	80
2	80	80
3	7	<23
4	56	32
5	148	25
6	-3	<21
7	59	37
8	-24	<19
9	-55	57
10	-24	28
11	-1	12

061

l	Fc	Fo
0	123	89
1	-65	37
2	52	51
3	224	186
4	22	44
5	72	58
6	79	90
7	48	85
8	106	115

111

l	Fc	Fo
0	845	637
1	251	195
2	418	361
3	272	232
4	448	281
5	501	425
6	293	331
7	293	352
8	246	280
9	91	147
10	161	179
11	154	159
12	163	179

l	Fc	Fo
13	155	136
14	98	104
15	84	96

l11

l	Fc	Fo
1	700	513
2	276	267
3	351	303
4	181	135
5	362	324
6	473	471
7	234	216
8	187	166
9	319	335
10	206	198
11	21	69
12	146	168
13	212	208
14	125	149
15	115	126
16	27	28

121

l	Fc	Fo
0	71	96
1	-190	225
2	-219	234
3	81	42
4	101	41
5	45	18
6	-20	44
7	-88	25
8	-53	55
9	-128	108
10	54	74
11	70	50
12	-39	< 9
13	-10	<21
14	-56	53
15	-20	<11

l21

l	Fc	Fo
1	-15	27
2	147	161
3	-26	42
4	-136	161
5	198	202
6	93	71
7	10	41
8	81	56
9	-241	182
10	-22	<25
11	180	136

l	Fc	Fo
12	-37	23
13	37	25
14	-5	32
15	-29	14

131

l	Fc	Fo
0	385	304
1	239	193
2	66	94
3	458	504
4	443	327
5	144	156
6	359	274
7	-26	14
8	170	191
9	459	352
10	33	41
11	70	97
12	141	99
13	39	55
14	128	122

l31

l	Fc	Fo
1	332	290
2	186	173
3	285	257
4	470	400
5	219	181
6	224	230
7	239	196
8	169	154
9	229	219
10	122	161
11	144	168
12	147	117
13	52	89
14	104	104
15	79	57

141

l	Fc	Fo
0	1	<23
1	-2	<23
2	-2	37
3	-2	30
4	56	76
5	52	78
6	17	19
7	-65	21
8	-33	<25
9	108	78
10	26	<21
11	6	32

l	Fc	Fo
12	40	<14
13	-23	< 7

l41

l	Fc	Fo
1	-33	25
2	-173	122
3	-116	78
4	80	62
5	-48	21
6	49	32
7	36	<25
8	-215	172
9	53	44
10	115	60
11	-54	25
12	1	<18
13	-56	78

151

l	Fc	Fo
0	216	173
1	160	124
2	205	173
3	151	161
4	146	89
5	153	145
6	36	65
7	76	90
8	148	182
9	63	83
10	56	103
11	66	51

l51

l	Fc	Fo
1	20	34
2	38	37
3	262	271
4	152	172
5	118	122
6	86	92
7	-11	<23
8	100	99
9	156	145
10	80	85
11	70	76

161

l	Fc	Fo
0	1	<21
1	144	104
2	-13	<19
3	-86	94
4	-45	73

l	Fc	Fo
5	-22	14
6	74	34
7	20	8

l61

1	168	140
2	75	76
3	-2	<19
4	-11	35
5	-14	<16
6	27	23
7	30	39
8	5	25

200

0	1111	1156
1	145	136
2	478	543
3	270	241
4	357	443
5	720	832
6	195	269
7	-39	<19
8	108	204
9	160	181
10	-17	34
11	-35	50
12	266	271
13	153	182
14	54	120
15	91	99

2o1

1	826	618
2	-80	76
3	142	181
4	-111	110
5	106	212
6	282	310
7	233	313
8	380	427
9	233	264
10	121	244
11	271	317
12	273	317
13	102	189
14	100	154
15	130	182
16	22	60

211

0	-597	513

l	Fc	Fo
1	521	462
2	256	213
3	328	306
4	319	255
5	118	60
6	238	212
7	247	232
8	144	122
9	70	58
10	11	<25
11	-29	28
12	10	<23
13	20	<21
14	14	<18
15	28	<12

211

1	604	443
2	-639	510
3	-224	136
4	-263	260
5	-208	138
6	52	71
7	-297	227
8	-268	234
9	-295	214
10	-209	179
11	82	58
12	-17	25
13	10	30
14	4	<21
15	-90	46
16	11	30

221

0	470	405
1	227	239
2	84	83
3	314	313
4	294	253
5	289	276
6	340	313
7	212	181
8	343	290
9	318	313
10	172	177
11	233	209
12	113	113
13	89	101
14	126	124

221

1	465	352

l	Fc	Fo
2	414	343
3	583	411
4	646	568
5	380	313
6	375	276
7	327	257
8	183	191
9	313	297
10	190	166
11	-58	30
12	50	65
13	166	135
14	149	113
15	124	106
16	82	60

231

0	12	27
1	-84	58
2	-219	145
3	-171	143
4	-67	32
5	-30	11
6	-90	83
7	-269	202
8	-264	170
9	21	18
10	142	101
11	-23	37
12	-53	27
13	-56	35

231

1	-27	42
2	-88	76
3	-6	39
4	168	122
5	173	115
6	148	83
7	149	101
8	132	78
9	141	83
10	69	64
11	-3	<23
12	33	<23
13	37	<19
14	8	<16
15	1	<11

241

0	194	170
1	198	172
2	291	239

l	Fc	Fo
3	304	242
4	182	136
5	87	89
6	91	73
7	103	94
8	132	103
9	46	42
10	24	34
11	93	71
12	28	35
	241	
1	247	181
2	124	372
3	145	53
4	186	175
5	136	127
6	182	159
7	99	78
8	-45	19
9	191	136
10	257	191
11	105	97
12	131	110
13	114	81
	251	
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2	98	67
3	113	51
4	4	<23
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6	86	65
7	58	44
8	62	41
9	54	32
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	$\bar{2}$51	
1	-42	34
2	181	122
3	-168	89
4	-108	87
5	3	<23
6	-66	23
7	20	<23
8	-150	99
9	-133	65
10	40	<18
11	-4	18

l	Fc	Fo
	261	
0	88	64
1	12	14
2	179	129
3	104	74
4	39	30
5	125	81
6	53	37
7	81	76
	$\bar{2}$61	
1	124	103
2	100	90
3	190	138
4	142	135
5	146	104
6	111	80
7	53	62
8	109	87
	311	
0	577	565
1	-7	46
2	350	322
3	355	304
4	427	396
5	440	437
6	185	211
7	236	237
8	213	244
9	115	179
10	144	165
11	162	172
12	170	179
13	103	104
14	59	76
	$\bar{3}$11	
1	999	839
2	190	115
3	201	179
4	511	478
5	279	280
6	310	297
7	346	306
8	172	166
9	347	349
10	355	352
11	3	46
12	88	120

l	Fc	Fo
13	222	225
14	124	150
15	139	158
16	65	76
	321	
0	55	62
1	-165	170
2	-123	71
3	222	195
4	-16	<18
5	103	92
6	-19	57
7	-270	212
8	120	170
9	143	115
10	-54	<23
11	-1	<23
12	-16	27
13	-28	<16
14	-3	<11
	$\bar{3}$21	
1	187	145
2	9	39
3	-77	44
4	-167	166
5	-61	27
6	259	260
7	35	51
8	-99	76
9	-61	55
10	15	<23
11	51	41
12	-72	41
13	73	60
14	75	23
15	-57	37
16	14	<11
	331	
0	200	168
1	256	200
2	200	179
3	264	266
4	140	156
5	172	188
6	139	110
7	-11	19
8	304	260
9	210	163

l	Fo	Fc
10	-12	9
11	134	136
12	49	37
13	66	85
	331	
1	138	127
2	339	241
3	284	207
4	176	156
5	226	223
6	226	191
7	124	127
8	180	163
9	167	143
10	43	97
11	134	152
12	123	97
13	93	110
14	107	110
15	40	37
	341	
0	56	25
1	81	69
2	19	19
3	-89	67
4	88	73
5	-3	18
6	-40	<23
7	41	39
8	-97	64
9	-6	<21
10	70	67
11	-6	<14
12	5	<5
	341	
1	17	<23
2	121	78
3	-167	142
4	-63	62
5	102	28
6	-35	41
7	113	46
8	-6	46
9	-115	87
10	37	<23
11	11	<21
12	1	<10
13	-42	39
14	-22	<5

l	Fo	Fc
	351	
0	232	193
1	224	191
2	231	204
3	113	104
4	104	96
5	168	154
6	156	120
7	121	97
8	74	97
9	121	154
	351	
1	140	149
2	-8	30
3	135	140
4	254	248
5	175	177
6	164	161
7	149	104
8	25	21
9	79	80
10	213	145
11	146	110
	361	
0	-17	18
1	8	34
2	-27	16
3	-10	16
4	-16	14
5	-5	12
6	50	30
	361	
1	24	<19
2	-16	<19
3	34	<19
4	29	<18
5	-22	<18
6	-17	<16
7	-29	<14
8	-3	<12
	401	
0	40	85
1	293	365
2	248	294
3	273	400
4	397	444

l	Fo	Fc
5	278	352
6	257	382
7	270	375
8	76	166
9	57	142
10	15	50
11	59	117
12	145	166
13	39	42
14	72	81
	401	
1	-181	304
2	220	289
3	275	289
4	38	35
5	179	234
6	108	147
7	238	331
8	302	375
9	273	343
10	434	563
11	86	140
12	-93	9
13	136	188
14	43	76
15	112	168
16	83	120
	411	
0	-242	168
1	-321	276
2	-238	154
3	30	44
4	-267	234
5	-160	136
6	16	76
7	17	30
8	22	42
9	-26	30
10	79	74
11	-32	9
12	-127	83
13	-19	7
14	-59	28
	411	
1	534	469
2	103	60
3	-55	19
4	-190	172
5	-219	181

l	Fc	Fo
6	213	175
7	55	<21
8	70	<21
9	72	<21
10	-177	150
11	177	152
12	270	175
13	25	<19
14	19	<19
15	-3	<19
16	-10	<14
	421	
0	488	359
1	144	106
2	293	271
3	284	290
4	306	312
5	362	322
6	76	65
7	19	41
8	278	258
9	246	216
10	216	198
11	199	184
12	80	87
13	117	115
	521	
1	930	807
2	576	430
3	369	273
4	497	393
5	320	251
6	351	329
7	336	267
8	137	108
9	172	161
10	186	161
11	173	140
12	166	129
13	176	143
14	207	168
15	137	106
16	113	78
	431	
0	94	80
1	127	133
2	184	159
3	175	120
4	134	127

l	Fc	Fo
5	36	23
6	-29	21
7	-50	21
8	-37	27
9	40	<23
10	58	41
11	16	<18
12	3	<14
	631	
1	-147	138
2	-90	62
3	-7	<19
4	1	<20
5	12	<21
6	5	<21
7	34	25
8	24	23
9	-50	<23
10	-90	53
11	-73	58
12	-104	53
13	-69	48
14	13	<16
15	27	7
	441	
0	105	90
1	120	97
2	210	216
3	154	138
4	74	64
5	140	113
6	95	97
7	175	140
8	236	158
9	-13	16
10	-56	25
11	57	37
	741	
1	147	117
2	-138	64
3	-48	32
4	287	188
5	173	147
6	120	106
7	113	115
8	55	67
9	200	126
10	162	120
11	47	74

l	Fc	Fo
12	86	74
13	68	69
	451	
0	-49	30
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2	-53	41
3	-129	83
4	-25	<21
5	22	28
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7	-51	12
8	21	41
9	79	69
	751	
1	63	42
2	151	76
3	-78	51
4	-89	82
5	48	<23
6	-31	16
7	90	28
8	21	41
9	-112	57
10	132	69
11	70	27
	461	
0	156	106
1	138	97
2	75	67
3	81	64
4	117	96
5	46	46
	761	
1	121	101
2	167	115
3	145	99
4	85	78
5	143	92
6	111	73
7	99	90
8	68	44
	511	
0	236	225
1	65	80
2	308	335

l	Fc	Fo
3	290	280
4	384	391
5	342	349
6	-4	9
7	120	152
8	294	271
9	119	136
10	71	106
11	150	135
12	105	106
13	70	83

511

l	Fc	Fo
1	538	512
2	331	292
3	246	195
4	381	317
5	350	324
6	157	142
7	199	179
8	280	271
9	253	262
10	281	260
11	111	133
12	73	76
13	164	152
14	69	97
15	127	140
16	128	120

521

l	Fc	Fo
0	164	184
1	21	74
2	54	112
3	112	124
4	-91	30
5	83	64
6	-87	87
7	-93	37
8	169	143
9	50	30
10	11	19
11	-18	21
12	65	62

521

l	Fc	Fo
1	341	283
2	53	18
3	-371	315
4	-23	41
5	-56	76
6	-13	9
7	106	71
8	-55	55
9	-54	50
10	28	<23
11	-12	30
12	-62	53
13	16	<21
14	40	<19
15	-8	<16
16	-17	<11

531

l	Fc	Fo
0	210	179
1	299	257
2	182	179
3	186	205
4	186	189
5	67	127
6	181	191
7	194	189
8	88	108
9	78	80
10	141	112
11	84	76

531

l	Fc	Fo
1	300	221
2	239	195
3	126	120
4	303	244
5	159	172
6	216	211
7	266	218
8	22	67
9	140	115
10	217	166
11	128	115
12	54	57
13	103	117
14	198	184
15	35	16

541

l	Fc	Fo
0	-30	<23
1	42	25
2	-27	57
3	-92	74
4	46	27
5	-3	<21
6	27	32
7	-79	50
8	-102	42
9	88	81
10	-15	<12

541

l	Fc	Fo
1	-89	53
2	174	122
3	177	115
4	-144	117
5	25	<23
6	59	<23
7	14	<23
8	95	50
9	10	<21
10	-37	<21
11	-19	<19
12	-3	<16
13	25	<14

551

l	Fc	Fo
0	80	112
1	135	145
2	178	163
3	76	65
4	60	50
5	118	83
6	89	58
7	189	115
8	125	129

551

l	Fc	Fo
1	122	158
2	144	159
3	47	58
4	58	76
5	205	163
6	163	129
7	140	117
8	104	80
9	0	<18
10	116	124
11	125	163

561

l	Fc	Fo
0	-2	46
1	-34	<14
2	19	37
3	22	62
4	9	21

l	Fc	Fo
	561	
1	-50	69
2	-31	50
3	-41	50
4	-45	23
5	2	<14
6	9	<14
7	-18	19
	601	
0	164	195
1	135	227
2	450	574
3	381	439
4	292	400
5	286	414
6	292	396
7	343	370
8	186	269
9	181	246
10	216	234
11	106	135
12	98	138
	601	
1	337	430
2	382	455
3	419	434
4	505	681
5	764	943
6	357	412
7	201	292
8	411	501
9	198	306
10	529	581
11	364	345
12	-239	214
13	78	106
14	219	179
15	118	136
16	191	227
	611	
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1	-257	244
2	22	<19
3	-113	110
4	-94	64
5	-14	50
6	-293	246
7	-36	19

l	Fc	Fo
8	141	110
9	30	35
10	83	76
11	-50	48
12	-41	<14
	611	
1	-159	129
2	-66	48
3	24	25
4	-76	58
5	-124	104
6	81	76
7	129	81
8	108	80
9	116	81
10	111	60
11	117	108
12	-5	<25
13	5	<23
14	40	<21
15	-15	<19
16	15	<14
	621	
0	81	94
1	185	173
2	161	154
3	181	184
4	262	273
5	53	69
6	-92	53
7	41	92
8	113	112
9	30	35
10	62	94
11	91	104
12	41	37
	621	
1	372	361
2	394	362
3	25	37
4	48	92
5	-6	65
6	51	96
7	169	181
8	14	46
9	93	90
10	117	110
11	73	119
12	179	170

l	Fc	Fo
13	152	127
14	104	133
15	53	89
16	21	34
	631	
0	82	90
1	124	142
2	118	115
3	63	67
4	38	46
5	28	41
6	36	76
7	64	71
8	32	14
9	-50	<19
10	-55	60
11	-6	<5
	631	
1	35	21
2	219	152
3	136	89
4	-129	90
5	-123	129
6	-3	<23
7	32	<25
8	15	<23
9	-122	92
10	-149	99
11	-20	41
12	-41	39
13	-69	58
14	35	16
15	53	42
	641	
0	203	170
1	234	207
2	142	131
3	72	67
4	165	145
5	213	181
6	144	110
7	196	156
8	230	165
9	64	71
	641	
1	185	170
2	61	61

l	Fc	Fo
3	112	94
4	336	251
5	283	251
6	232	221
7	230	193
8	136	112
9	196	124
10	148	124
11	75	87
12	116	74
13	53	53
	651	
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1	-28	14
2	-115	83
3	-3	<19
4	-1	<18
5	-53	16
6	6	<14
7	-87	60
	851	
1	9	<21
2	2	30
3	-78	89
4	-35	39
5	68	19
6	4	<19
7	14	<19
8	37	<18
9	14	<16
10	51	35
11	53	50
	661	
0	120	145
1	44	81
2	83	85
	361	
1	126	161
2	61	85
3	43	34
4	4	32
5	66	76
6	24	21
	711	
0	167	159

l	Fc	Fo
1	152	182
2	278	313
3	211	230
4	258	289
5	147	133
6	-2	14
7	180	209
8	188	191
9	91	101
10	110	115
11	63	57
	711	
1	211	205
2	185	173
3	368	256
4	283	196
5	216	181
6	223	177
7	113	101
8	189	193
9	180	150
10	197	191
11	221	209
12	55	78
13	69	76
14	115	65
15	83	46
16	116	44
	721	
0	80	103
1	19	51
2	73	85
3	-16	<23
4	-139	104
5	-14	<23
6	32	51
7	-7	<23
8	-36	<21
9	50	53
10	34	<16
11	-83	42
	721	
1	82	57
2	115	104
3	-26	27
4	-31	28
5	-47	57
6	-7	23
7	5	<23

l	Fc	Fo
8	71	28
9	95	44
10	-42	42
11	-49	42
12	20	<25
13	31	<19
14	-45	34
15	-11	<14
	731	
0	99	117
1	274	212
2	87	87
3	177	179
4	217	214
5	107	135
6	162	161
7	106	101
8	81	119
9	83	94
10	70	50
	731	
1	302	242
2	437	381
3	-143	58
4	137	149
5	368	312
6	91	136
7	261	257
8	133	143
9	45	64
10	220	156
11	153	112
12	100	83
13	93	90
14	116	122
	741	
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1	60	62
2	-5	<23
3	-17	<21
4	53	48
5	31	14
6	-27	<18
7	-19	<16
8	86	78
	741	
1	-12	27

l	Fc	Fo
2	17	<23
3	64	16
4	-14	27
5	-48	53
6	-57	55
7	5	<23
8	19	<21
9	-28	<21
10	-7	<19
11	0	<18
12	-26	34
13	-46	11

751

l	Fc	Fo
0	67	62
1	71	69
2	120	104
3	52	46
4	52	44
5	26	27

751

l	Fc	Fo
1	98	96
2	90	90
3	122	90
4	59	32
5	92	71
6	127	96
7	67	41
8	108	96
9	95	65
10	57	55

761

l	Fc	Fo
0	12	23

761

l	Fc	Fo
1	-75	62
2	51	11
3	36	11
4	-87	74

801

l	Fc	Fo
0	-106	74
1	133	251
2	262	379
3	109	230
4	307	419
5	-48	46
6	-103	50
7	323	414
8	180	255
9	124	253
10	131	189

801

l	Fc	Fo
1	323	407
2	405	524
3	246	377
4	276	405
5	444	570
6	333	393
7	7	50
8	135	244
9	166	248
10	145	248
11	198	246
12	25	27
13	67	67
14	125	152
15	84	129
16	153	158

811

l	Fc	Fo
0	172	147
1	119	108
2	100	69
3	79	71
4	112	81
5	-40	44
6	-142	74
7	80	77
8	88	37
9	17	25
10	41	23

811

l	Fc	Fo
1	-182	154
2	-167	145
3	-165	145
4	-116	97
5	39	<23
6	49	27
7	-135	110
8	-18	<23
9	-14	<25
10	-45	<25
11	123	92
12	-153	115
13	-240	131
14	0	<19
15	-38	30

l	Fc	Fo
	821	
0	236	225
1	243	244
2	163	168
3	274	266
4	169	147
5	118	127
6	176	149
7	110	92
8	53	44
9	14	18
10	61	35

821

l	Fc	Fo
1	138	142
2	193	207
3	25	32
4	79	60
5	216	196
6	102	127
7	168	156
8	151	147
9	114	122
10	242	216
11	211	196
12	90	101
13	88	71
14	120	117
15	51	46

831

l	Fc	Fo
0	16	30
1	-30	<23
2	-93	55
3	-142	87
4	-4	<23
5	44	46
6	-15	<19
7	13	35
8	36	53

831

l	Fc	Fo
1	63	46
2	291	234
3	237	156
4	-44	41
5	-111	101
6	-17	55
7	51	25
8	79	23
9	32	21

l	Fc	Fo
10	-10	28
11	22	<21
12	39	<19
13	52	<16
14	67	37
	911	
0	107	120
1	217	235
2	234	207
3	159	147
4	128	120
5	50	50
6	125	110
7	143	120
8	73	97
9	127	104
	911	
1	150	136
2	202	179
3	216	200
4	171	136
5	224	177
6	256	204
7	114	115
8	122	122
9	102	124
10	128	120
11	274	209
12	109	83
13	17	<19
14	126	97
15	124	90
	921	
0	35	28
1	26	<23
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5	-18	<21
6	10	<19
7	10	<18
8	-9	<11
9	-1	<7
	921	
1	4	<23
2	-117	73
3	137	106

l	Fc	Fo
4	205	156
5	-173	129
6	-33	34
7	39	<23
8	-18	<23
9	113	65
10	-25	23
11	-8	<21
12	34	<19
13	-66	41
14	-2	<14
15	8	<5
	931	
0	148	106
1	111	67
2	10	18
3	191	158
4	157	106
5	48	41
6	43	60
7	127	119
	931	
1	69	78
2	269	251
3	79	89
4	-15	23
5	194	172
6	117	149
7	145	156
8	142	126
9	75	55
10	129	83
11	68	53
12	71	87
13	124	80
	1001	
0	36	58
1	170	216
2	106	126
3	147	221
4	116	90
5	-217	253
6	2	34
7	193	216
8	48	62
	1001	
1	119	129

l	Fc	Fo
2	159	232
3	162	218
4	215	248
5	71	113
6	15	81
7	61	81
8	46	81
9	27	65
10	66	76
11	39	57
12	44	78
13	161	173
14	90	92
15	35	73
	1011	
0	131	131
1	-36	<25
2	41	37
3	-23	<23
4	-59	<21
5	102	90
6	16	<18
7	-89	51
8	-35	21
	1011	
1	-39	23
2	105	48
3	57	<23
4	100	51
5	57	28
6	110	55
7	11	<25
8	-85	55
9	81	28
10	-5	<23
11	-34	<21
12	1	30
13	-71	83
14	-15	19
	1021	
0	219	202
1	156	143
2	125	115
3	172	184
4	153	152
5	194	168
6	165	168
7	115	115

l	Fc	Fo
	I,2,1	
1	138	156
2	168	168
3	89	94
4	44	32
5	314	266
6	339	204
7	165	156
8	165	133
9	153	127
10	151	140
11	266	235
12	174	154
13	-9	<14
14	56	34
	1,3,1	
0	19	19
1	2	<21
2	-44	25
3	-65	41
4	13	<18
5	25	<14
6	-5	<11
	I,3,1	
1	-33	28
2	9	<23
3	2	<23
4	-55	60
5	-56	57
6	-69	60
7	-63	55
8	-4	<21
9	25	<19
10	35	<16
11	22	<16
12	4	<14
	1,1,1	
0	131	133
1	149	138
2	116	110
3	163	152
4	55	46
5	0	25
6	141	127
	I,1,1	
1	72	80
2	198	165
3	176	156
4	-13	<23
5	153	127
6	285	214
7	92	103
8	78	76
9	85	74
10	70	71
11	181	136
12	116	99
13	43	25
	1,2,1	
0	82	65
1	-75	46
2	-40	19
3	47	46
4	45	41
5	-23	<12
6	-15	< 7
	I,2,1	
1	-59	73
2	-25	32
3	5	<23
4	122	69
5	-48	44
6	-38	46
7	18	<21
8	-90	67
9	29	<19
10	-12	<18
11	5	<16
12	88	44
13	-111	69
	1,3,1	
0	98	87
1	55	55
2	107	112
3	91	85
4	53	35
	I,3,1	
1	107	92
2	70	81
3	94	115
4	158	170
5	94	73
6	53	56
7	134	131
8	96	73
9	95	83
10	94	65
11	64	35
	1,0,1	
0	168	235
1	178	253
2	180	221
3	82	122
4	79	69
	I,0,1	
1	183	212
2	103	147
3	139	182
4	118	122
5	73	53
6	131	179
7	93	119
8	154	168
9	111	119
10	28	28
11	175	179
12	162	161
	1,1,1	
0	2	<19
1	-94	90
2	-17	30
3	-74	50
4	52	58
	I,1,1	
1	-27	21
2	76	48
3	37	48
4	211	163
5	99	69
6	-131	64
7	19	<21
8	13	<19
9	5	<19
10	62	<18
11	-34	23
12	-25	19
	1,2,1	
0	77	89
1	32	39
2	25	48
3	89	92

l	Fc	Fo
4	27	< 7

$\bar{1}221$

1	19	42
2	82	94
3	120	133
4	43	69
5	89	126
6	193	251
7	154	177
8	36	55
9	45	67
10	51	60
11	54	58

1231

0	11	16
1	23	39

$\bar{1}231$

1	-20	35
2	-78	85
3	-92	87
4	-42	60
5	-8	23
6	0	<16
7	-5	16
8	-22	14
9	-26	14

1311

0	102	97
1	39	34
2	91	92

$\bar{1}311$

1	112	119
2	84	96
3	120	113
4	32	25
5	39	27
6	175	165
7	101	108
8	79	69
9	86	51
10	27	27

$\bar{1}321$

1	-78	83
2	5	16

l	Fc	Fo
3	52	<16
4	-15	19
5	-22	19
6	42	<16
7	27	<14
8	-70	58
9	-21	12
10	15	< 7

$\bar{1}4,01$

2	63	124
3	114	131
4	35	48
5	-125	127
6	205	241
7	223	200
8	35	64

$\bar{1}411$

3	-46	16
4	7	<12
5	20	<12
6	-98	67
7	-85	48

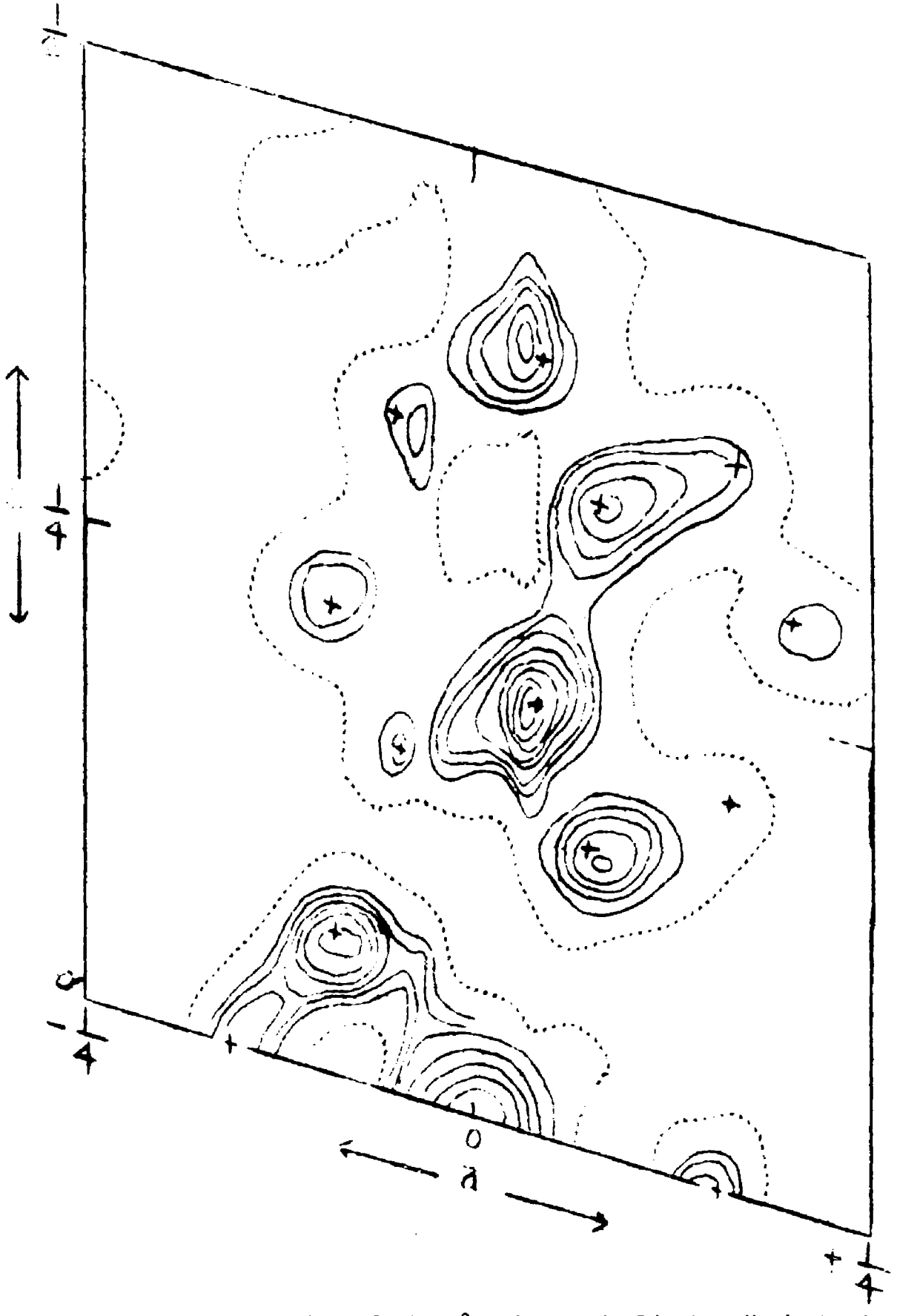

Figure 1. Patterson Projection of Zinc 8-Hydroxyquinolinate Dihydrate Upon (010). Compare With Figures 2 and 3. Crosses Indicate Final Positions of Atom Centers. Contour lines at arbitrary intervals, zero contour dotted, contours around origin at 4x value of others.

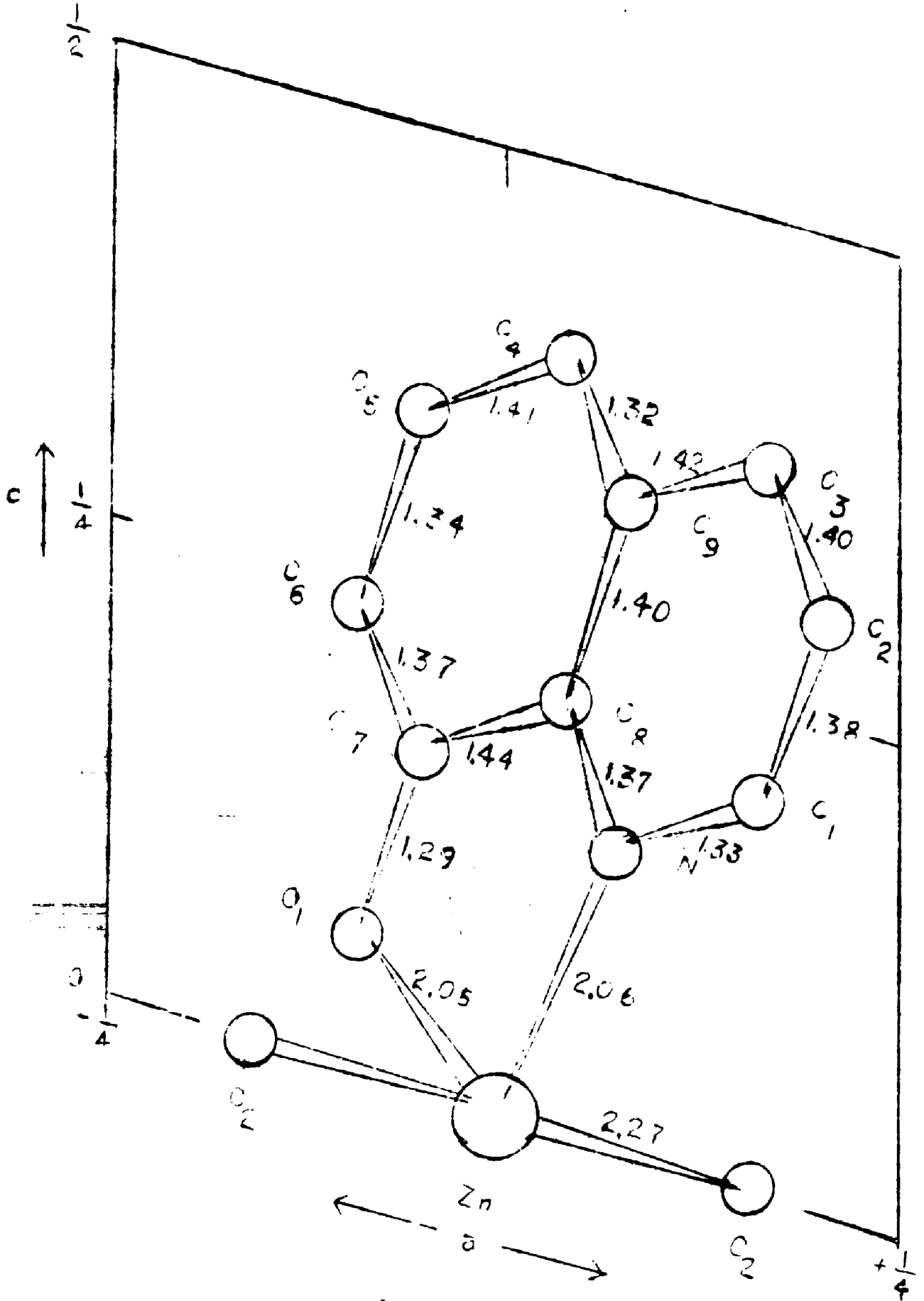

Figure 3. Structure of Zinc 8-Hydroxyquinolinate Dihydrate as Seen Projected upon (010). Actual Interatomic Distances Indicated in Angstrom Units.

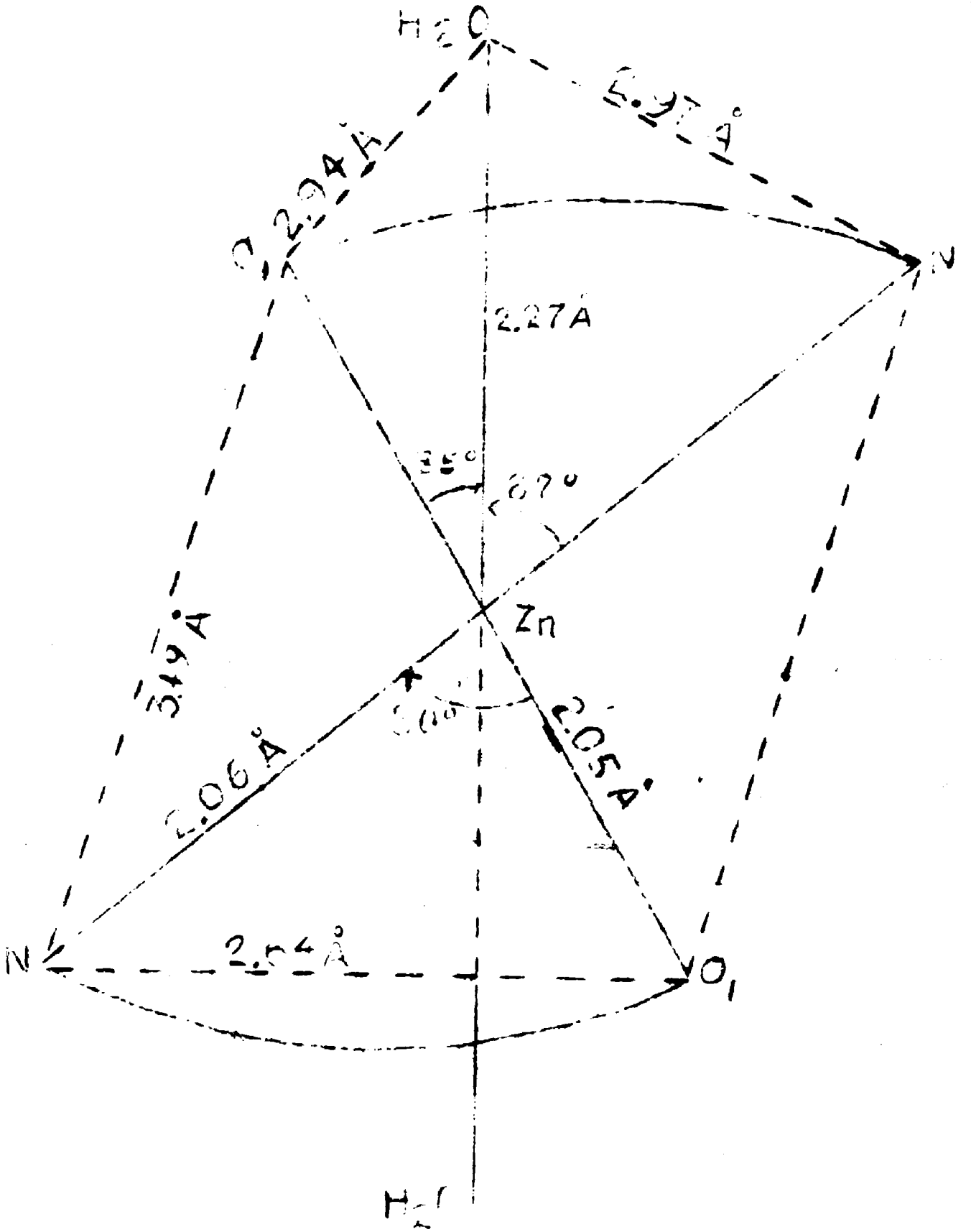

Figure 4. Schematic Representation of Bonds Around Central Zinc Atom in Zinc 8-Hydroxyquinolinate Dihydrate.